

Synthesis and Characterization of High-T_c Screen-Printed Y-Ba-Cu-O Films on Alumina

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SYNTHESIS AND CHARACTERIZATION OF HIGH- T_c SCREEN-PRINTED
Y-Ba-Cu-O FILMS ON ALUMINA

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SUMMARY

Thick films of $YBa_2Cu_3O_{7-x}$ have been deposited on highly polished alumina substrates by the screen printing technique. To optimize the post-printing heat treatment, the films were baked at various temperatures for different lengths of time and oxygen-annealed at a lower temperature. The resulting films were characterized by electrical resistivity measurements, x-ray diffraction, and optical and scanning electron microscopy. Properties of the films were found to be highly sensitive to the post-printing thermal treatment. Films baked for 15 min at 1000 °C in oxygen were hard, adherent, near single phase, and superconducting with $T_c(\text{onset}) \sim 96$ K, $T_c(\text{zero}) \sim 66$ K and ΔT_c (10 to 90 percent) ~ 10 K.

INTRODUCTION

Films of high- T_c perovskite superconductors (ref. 1) are needed for fundamental research and for various engineering applications. A variety of techniques have been employed for the deposition of thin films of these materials. These include: molecular beam epitaxy (refs. 2 and 3), electron beam evaporation (refs. 4 and 5), sputtering (refs. 6 to 8), laser ablation, (refs. 9 and 10), sequential metal layer evaporation, (refs. 11 and 12), metallorganic chemical vapor deposition (ref. 13), and plasma spraying (refs. 14 and 15). All of these methods require quite sophisticated facilities. Films have also been prepared using relatively simple and inexpensive techniques such as dip coating, spinning, and spraying homogenous solutions of inorganic metal salts (nitrates (refs. 16 and 17) or acetates (ref. 18)), metallorganics (neodecanoates (ref. 19) or 2-ethyl hexanoates (ref. 20)), or naphthenates (ref. 21). The sol-gel approach has also been applied for the deposition (refs. 22 and 23) of thick films.

A simple and promising technique for depositing thick films is that of screen printing (refs. 24 and 25). An additional advantage of this method over some others is that the electronic and microwave circuit patterns and devices are directly printed, thus avoiding the etching step. This is of particular significance in the case of the Y-Ba-Cu-O superconductor which is highly reactive (ref. 26) with moisture and other chemicals.

In this paper, we report on the screen printing of high- T_c films of $YBa_2Cu_3O_{7-x}$ on alumina, a very widely used and technologically interesting substrate material in the electronic industry. The objective of this work was to optimize the post-printing thermal treatment in order to obtain good superconducting films. The films were characterized by x-ray diffraction (XRD), optical and scanning electron microscopy (SEM), and resistivity measurements.

EXPERIMENTAL

The superconducting $YBa_2Cu_3O_{7-x}$ powder was prepared from Y_2O_3 (Molycorp 99.99 percent), $BaCO_3$ (ALFA technical grade), and CuO (ALFA ACS grade) powders by the solid state reaction method following a procedure which was essentially the same as that described previously (ref. 26). This powder was passed through a 500 mesh screen and mixed thoroughly with an appropriate amount of an organic vehicle to form a paste which was printed directly on high purity alumina substrates (superstrate 996 from Materials Research Corporation) through a 325 mesh stainless steel or silk screen. The films were oven-dried at 300 to 350 °C for 1.5 to 2 hr. They were then heated at 5 °C/min to the sintering temperature, held for various lengths of time, cooled at 3 °C/min to 450 °C, annealed for 3 hr, and finally slow cooled to ambient temperature. The complete sintering and annealing cycle was carried out in flowing oxygen. To optimize the post-printing heat treatment, the baking temperature and time were varied from 900 to 1000 °C, and 5 min to 4 hr, respectively. The film thickness was ~30 to 50 μm as determined using a surface profile measuring system (Dektak II-D, Sloan Technology Corporation). The films fired at or above 980 °C were hard and displayed good adhesion to the substrate.

The phases present in the baked films were identified from XRD measurements which were carried out using a Phillips ADP-3600 automated diffractometer equipped with a crystal monochromator employing $CuK\alpha$ radiation in the 2θ range 10 to 80°. The film microstructure was observed in an optical microscope and an SEM. Resistivity and its temperature dependence were measured in the standard four-probe configuration down to liquid helium temperature. Silver paint was used to attach the leads.

RESULTS AND DISCUSSION

The sintering conditions, physical appearance, phases present, resistive transition temperature, T_c , and transition width (10 to 90 percent), ΔT_c , etc. for various films are listed in table I. Films number 1, 2, 3, B4, and B7 had very poor adhesion and peeled off from the substrate during resistivity measurements. The temperature dependence of resistivity for some of the films normalized to its value at 100 K are presented in figure 1. The resistance increases with decrease in temperature (semiconducting behavior) from room temperature to the onset temperature, $T_c(\text{onset})$, where a sharp drop occurs. Film number 6 which had been fired for 4 hr at 945 °C had $T_c(\text{onset}) \sim 93$ K, $T_c(\text{zero}) \sim 77$ K, and ΔT_c (10 to 90 percent) ~ 6 K but had very poor adhesion with the substrate. Film number B8 which was sintered at 970 °C for 1 hr only became fully superconducting at ~ 45 K and number B6 only at ~ 30 K. Films number B5 and B6 lost 90 percent of their resistivity by 76 and 58 K, respectively, but did not become fully superconducting even at 4 K. Resistivity measurements on film number 8 were not carried out below 77 K and the resistance of film

number B3 did not become zero even in liquid helium. Only those films fired at 1000 °C displayed excellent adhesion with the substrate. The temperature dependences of their normalized resistivity are depicted in figure 2. Film number 4, fired for 30 min, had some greenish regions whereas the other two films (number B1 and 5) were entirely black. Various characteristics of these films are listed in table I. From these results the optimum firing temperature and time are found to be 1000 °C and 15 min, respectively. Film number 5 which was baked under these conditions displayed the best characteristics with $T_C(\text{onset}) = 96$ K, $T_C(\text{zero}) = 66$ K, and $\Delta T_C = 10$ K. Films fired for shorter or longer times at 1000 °C were of poorer quality. The large transition widths of those fired for longer times may be due to the interdiffusion of aluminum into the superconducting film, as reported by other researchers (refs. 5 and 16). Alumina is reported (ref. 27) to have a limited solubility in $\text{YBa}_2\text{Cu}_3\text{O}_7$ but chemically decomposes it. The T_C of the unreacted $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase remain unchanged but the ΔT_C becomes large probably due to impurities from the decomposition products.

Some of the films were observed in the optical microscope. The grid pattern of the printing screen was visible in B2, fired for 5 min at 990 °C. Film fired for 15 min at 1000 °C was smooth as shown in optical micrographs in figure 3. SEM micrographs of some of the films are presented in figure 4.

Figure 5 shows the XRD patterns of some of the films. In figure 6, the XRD profiles of films fired at 1000 °C for 5 and 15 min are compared with those for a bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample. All the diffraction lines of the perovskite superconducting phase are present in the films. The most prominent lines for Y_2BaCuO_5 at $d = 2.989, 2.923, 2.824\text{\AA}$ are also present in some of the films. However, the intensities of these peaks, labelled as Y, are very weak. These results indicate that the films prepared in the present study consist of single phase material along with small concentrations of impurities.

Koinuma et al. (ref. 25) were not successful in the preparation of superconducting Yb-Ba-Cu-O films on alumina substrates by screen printing. Budhani et al. (ref. 24) did obtain superconducting Y-Ba-Cu-O films on sapphire and alumina substrates by screen printing and baking for 30 min at 1000 °C in oxygen which resulted in phase separation. BaCuO_2 , $\text{Y}_2\text{Cu}_2\text{O}_5$, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phases were reported to be present in their multiphase films. In contrast, the films fabricated in the present study contained nearly single phase material. The (considerable) effect of substrate material on the characteristics of the films is being investigated and will be reported elsewhere.

In conclusion, we have demonstrated that nearly single phase high- T_C superconducting films can be fabricated using a simple screen printing technique. The film properties are strongly dependent on the post-printing thermal treatment. Optimum baking condition as judged by film adherence and transition temperature was found to be 1000 °C for 15 min in flowing oxygen. However, films with higher $T_C(\text{zero})$, but poor adhesion were formed at 945 °C. Thus techniques for improving film adhesion at lower firing temperatures need to be investigated.

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TABLE I. - CHARACTERISTICS OF $YBa_2Cu_3O_{7-x}$ FILMS SCREEN PRINTED ON Al_2O_3 SUBSTRATES, FIRED UNDER DIFFERENT CONDITIONS, AND OXYGEN ANNEALED AT 450 °C FOR 3 HR

Film number	Sintering		T_C (K)			ΔT_C (K), 10 to 90 percent	Adhesion
	Temperature, °C	Time	Onset	Midpoint	Zero		
1	900	4 hr	--	--	---	--	Very poor*
2	920	2 hr	--	--	---	--	Very poor*
6	945	4 hr	93	90	77	6	Poor
3	950	1 hr	--	--	---	--	Poor*
7	960	2 hr	95	90	<77	9	Poor
B-7	970	0.5 hr	--	--	---	--	Poor*
B-8	970	1 hr	95	88	44	18	Poor
B-4	980	5 min	--	--	---	--	Very poor*
B-5	980	15 min	98	90	---	18	Fair
B-6	980	30 min	93	83	---	38	Fair
8	980	1 hr	92	--	---	--	Good
B-2	990	5 min	92	--	---	--	Fair
B-3	990	15 min	93	87	---	--	Good
B-1	1000	5 min	94	80	37	36	Excellent
5	1000	15 min	96	89	66	10	Excellent
4	1000	30 min	93	88	60	16	Excellent

*Film peeled off from substrate during resistivity measurements.

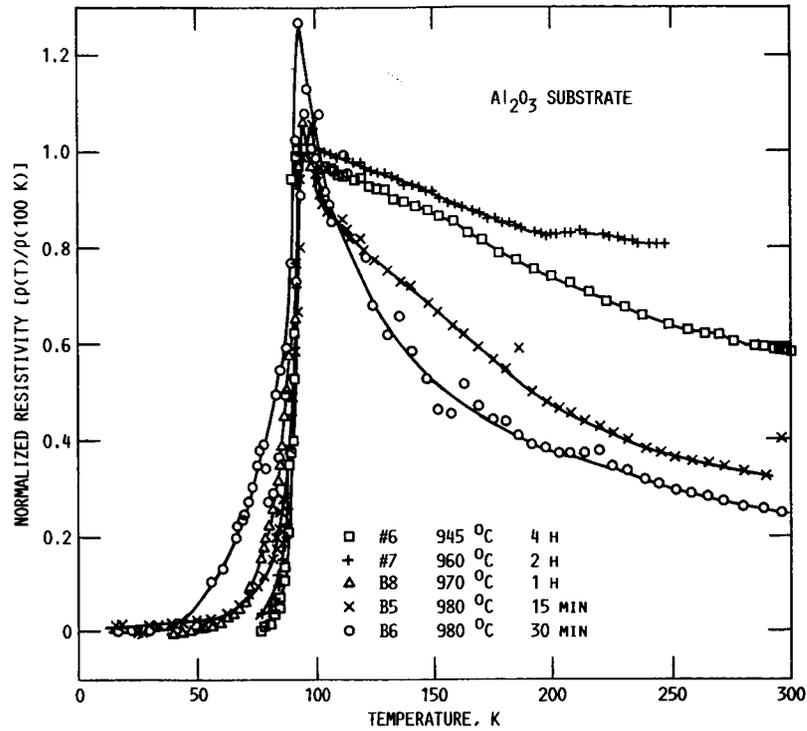


FIGURE 1. - TEMPERATURE DEPENDENCE OF ELECTRICAL RESISTIVITY OF $YBa_2Cu_3O_{7-x}$ FILMS SCREEN PRINTED ON ALUMINA SUBSTRATES AND FIRED AT THE INDICATED TEMPERATURES AND TIMES.

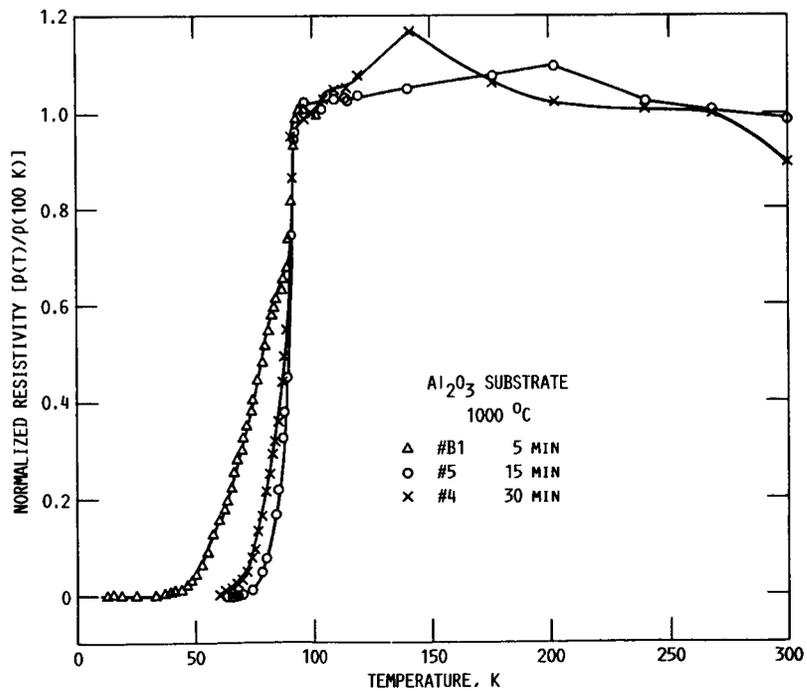
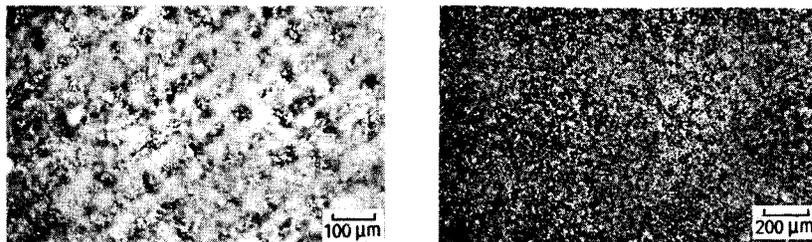


FIGURE 2. - ELECTRICAL RESISTIVITY VERSUS TEMPERATURE CURVES FOR $YBa_2Cu_3O_{7-x}$ FILMS ON ALUMINA SUBSTRATES SINTERED AT 1000 °C FOR VARIOUS TIMES IN FLOWING OXYGEN.

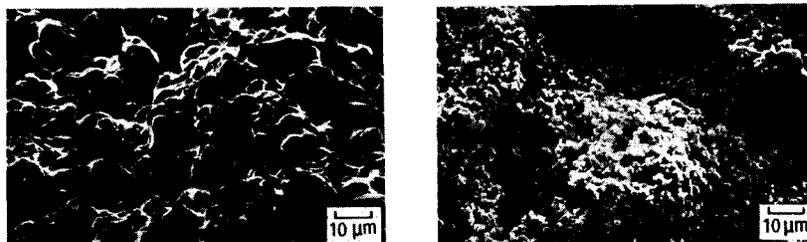
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(a) 990 °C, 5 MIN.

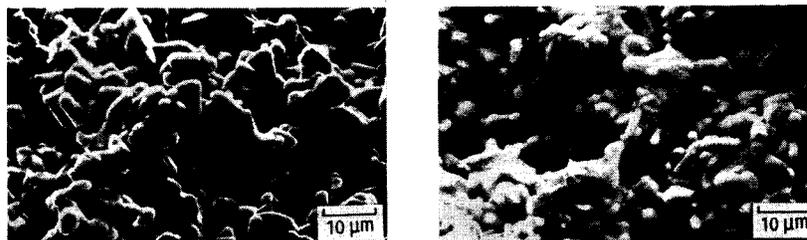
(b) 1000 °C, 15 MIN.

FIGURE 3. - OPTICAL MICROGRAPHS OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ FILMS ON ALUMINA SUBSTRATES BAKED IN OXYGEN.



(a) 980 °C, 1 hr.

(b) 990 °C, 5 MIN.



(c) 1000 °C, 15 MIN.

(d) 1000 °C, 30 MIN.

FIGURE 4. - SCANNING ELECTRON MICROGRAPHS OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ FILMS SCREEN PRINTED ON ALUMINA SUBSTRATES AND FIRED IN OXYGEN.

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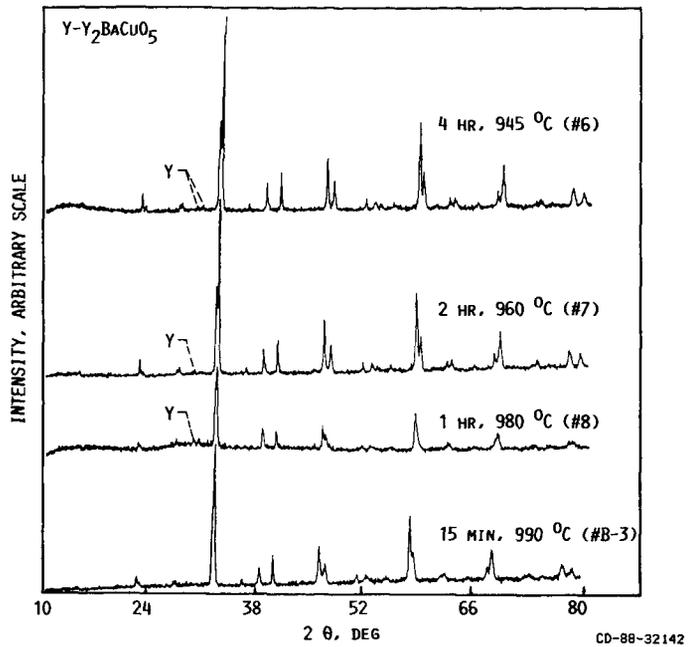


FIGURE 5. - X-RAY DIFFRACTION SPECTRA OF YBa₂Cu₃O_{7-x} FILMS SCREEN PRINTED ON ALUMINA SUBSTRATES AND BAKED AT THE INDICATED TEMPERATURES AND TIMES. THE UNLABELLED PEAKS ARE FOR THE SUPERCONDUCTING PEROVSKITE PHASE.

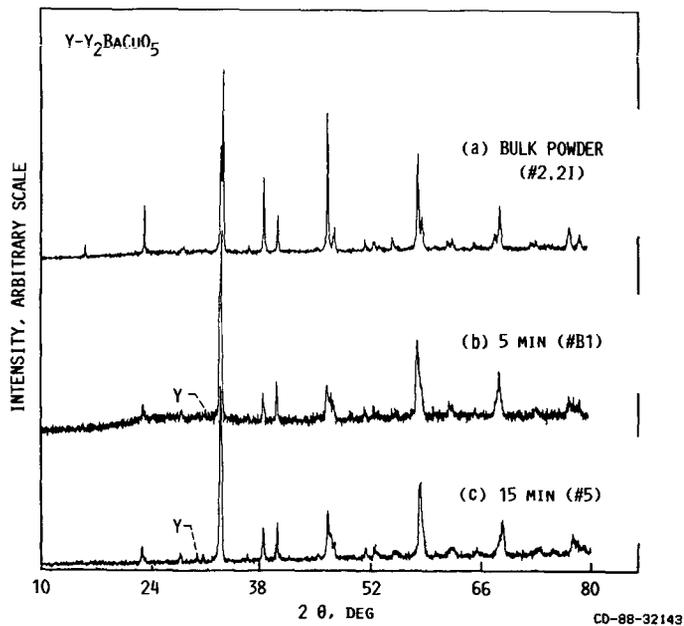


FIGURE 6. - X-RAY DIFFRACTOGRAMS OF YBa₂Cu₃O_{7-x} (a) BULK POWDER, AND FILMS SCREEN PRINTED ON ALUMINA SUBSTRATES AND FIRED AT 1000 °C FOR (b) 5 AND (c) 15 MIN IN OXYGEN.



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